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Transesterification of vegetable oil to biodiesel over Mgo-Li_2O catalysts templated by a PDMS-PEO comb-like copolymer

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Abstract

In this study, the preparation of MgO-Li_2O catalyst for biodiesel synthesis using PDMS–PEO as a structure-directing agent has been investigated. Compared to the catalysts reported so far, LM0.12-873 (Li/Mg molar ratio=0.12, calcination temperature is 873 K) exhibited an excellent performance and showed great potential in industrial application. The synergistic effect of macro- and mesopores on the templated catalysts functioned efficiently as a catalyst for transesterification. The basic strength of MgO-Li_2O catalysts was enhanced due to the lattice distortion and defects created by the substitution of the Li ions in MgO lattice. The catalytic activities of MgO-Li_2O depend on the amount of strong base sites with the most active catalyst of LM0.12-873 exhibiting the largest amount strong base sites.

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Keywords: biodiesel; catalyst; leaching; templated; Transesterification

1. Introduction

Biodiesel can be produced through transesterification of vegetable oils and fats with methanol in the presence of a suitable catalyst [1]. The conventional catalysts for this transesterification reaction are homogeneous strong bases or homogeneous acids [2]. Due to their fast reaction rates and less corrosive properties, bases are preferred to acid catalysts. Unfortunately, removal of the base after reaction is problematic [3]. Therefore, efforts in recent years have been directed towards to the development of heterogeneous catalyst systems to produce biodiesel [4].

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There are many solid heterogeneous acid- and alkali-catalysts for biodiesel synthesis. Generally, the performances of these acid catalysts are inferior to the base catalysts. For this reason, a wide variety of solid bases such as alkali earth oxides, hydrotalcites, alkali-doped oxides, mixed metal oxides, have been examined for biodiesel synthesis [5]. In our previous studies, the heterogeneous alkali-catalysts of Li-doped MgO, CaO-CeO_2 mixed oxides, and TiO_2-MgO mixed oxides were prepared and used to produce biodiesel [6-8]. However, the catalytic activities and stabilities need to be further promoted. Our Li-doped MgO produced the high biodiesel yield (93.9%) within 2 h at 333 K, but metal leaching was significant [6]. To reduce the leaching, we prepared TiO_2-MgO mixed oxides which achieved lower Mg and Ti leaching of 19 and 7 ppm. But, the reaction temperature was as high as 423 K with a low biodiesel yield of 79.9% [7]. At 373 K, our CaO-CeO_2 mixed-oxide catalyst produced 80.0% biodiesel yield, but the Ca leaching reached 33 ppm [8]. To date, it is still a challenge to search an active and stable solid catalyst, which could yield products under mild reaction conditions (lower temperature and pressure at the level of high biodiesel yield).

Our previous reports revealed that the doped or mixed oxides catalysts showed remarkably higher catalytic activities than un-doped or un-mixed catalyst due to the defects induced by the substitution of two metal ions on the surface. However, an impregnation method was taken in our previous studies, resulting in aggregation of metal species on the surface of the catalysts. This aggregation enhanced metal leaching and deteriorated the stability of catalysts. Jeon et al. reported the synthesis of mesoporous MgO catalyst using an amphiphilic comb-like copolymer, poly(dimethylsiloxane-ethylene oxide) (PDMS-PEO) as a structure-directing agent [9]. By templating micelles of PDMS-PEO copolymer, mesoporous MgO with a high surface area was generated after calcination at 500°C. Therefore, it should be interesting to tailor the structures of mixed oxides catalysts by templating micelles of PDMS-PEO. However, no report on templated catalysts of mixed oxides for biodiesel synthesis can be found.

In this study, the preparation of MgO-Li_2O catalyst for biodiesel synthesis using PDMS–PEO as a structure-directing agent has been investigated. The effects of the Li/Mg molar ratio were studied. The anti-leaching abilities of catalysts were addressed.

2. Experimental

2.1. Catalysis synthesis

An aqueous solution of MgO-Li_2O precursor was prepared by dissolving $Mg(NO_3)_2 \cdot 6(H_2O)$ and $LiNO_3$ in distilled water, then adding PDMS-PEO and of NH_4OH. NH_4OH was used to adjust the pH to around 10.5. This transparent colourless solution was kept in an autoclave at 433 K for 24 h. Then, it was kept in a drying oven at 363K to evaporate the solvent and became a gel-like solid. Finally, all samples were crystallized into MgO-Li_2O nanoparticles by calcination at the temperature ranging from 823 to 923 K for 4 h with a ramping rate of 4 K min^{-1} under air. The catalysts thus prepared by the method above are hereafter denoted as LMA-B, where A is the Li/Mg molar ratio and B is the calcination temperature (K).

2.2. Catalytic testing

All the transesterification reactions were performed in a 100 ml three-neck round bottom flask equipped with a reflux condenser and an agitated stirrer. The reaction procedure was as follows: First, the catalyst was dispersed in methanol under agitation. Then the soybean oil was added into the mixture and heated under vigorous stirring at a fixed speed of 800 rpm during each reaction test. After reaction, the catalyst was separated from the biodiesel product by centrifugation and the excessive amount of methanol was evaporated under reduced pressure in a rotary evaporator. The yields of biodiesel were analyzed using a gas chromatograph (FULI9790, China) equipped with a flame ionization detector (FID) detector and a capillary column (30QC3/AC20-0.5, 30m×id0.32 μm, SGE, Australia).

2.3. Catalysts characterization

For the leaching measurements, the catalyst was separated and centrifuged from the liquid reaction mixture after the completion of reaction, and then the liquid mixture was analyzed using ICP-AES (TJA IRIS 1000) to measure the alkali content.

The catalyst samples were analyzed using a JEOL JSM 6360M scanning electron microscope (SEM). The crystal phase was identified by means of X-ray powder diffraction (XRD) using a Rigaku D/max 2550VB/PC. X-ray photoelectron spectra (XPS) experiments were carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg Ka radiation ($h\nu$ = 1253.6 eV). The surface basicity of the templated catalysts were characterized by temperature programmed desorption (TPD) of CO_2 on Micrometrics AutoChem II 2920 System.

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3. Results and discussion

3.1. Catalytic activity

The effect of the Li/Mg molar ratio on the biodiesel yield is shown in Table 1. The specific surface areas and pore size are also given. Compared to the low biodiesel yield of 5.50%, the addition of Li greatly increased the biodiesel yield of parent MgO. The LM0.12-873 exhibited the highest biodiesel yield of 96.2% at 333 K. The catalyst surface area decreased from 94.7 to 23.7 $m^2\ g^{-1}$ with the Li/Mg molar ratio increasing from 0 to 0.16. A similar decrease in MgO surface area during the doping by Li was also reported by Wen et al. [6]. This is most likely attributed to $LiNO_3$ melting during the thermal decomposition of the resulting $LiNO_3/Mg(NO_3)_2$ solid [10]. The pore sizes of the samples with different Li/Mg molar ratios were stabilized at around 30 nm. It is well known that the decrease of the specific surface area is unfavorable for most catalysis reactions. However, in this case, the LM0.12-873 was the most active catalyst, which is likely related to the changes of the basic sites and strength on the surfaces of the catalysts by altering Li/Mg molar ratio. As presented in Table 1, LM0.08-873 showed the highest Mg leaching of 12 ppm. The highest Li leaching of 2.2 was observed for LM0.16-873. The effects of the Li/Mg molar ratio on the metal leaching is complicated. On balance LM0.12-873 exhibited the best anti-leaching performance with next to the lowest Mg and Li leaching values. Since quality standards of biodiesel such as EN14214 limit the alkali metal or alkali earth metal content to 5 ppm, the good anti-leaching performance of LM0.12-873 (1.3 and 1.6 ppm for Li and Mg leaching, respectively) means that the removal of the soluble metal species (e.g. by cation-exchange resin) to purify the produced biodiesel are not needed any more.

Table 1 Composition, surface area and catalytic results of templated catalysts

Catalyst	Li/Mg molar ratio	Calcination Temperature (K)	BET ($m^2\ g^{-1}$)	Pore size (nm)	leaching (ppm)		Biodiesel Yield (%)
					Li	Mg	
MgO	0	873	94.7	29.6	0	2.7	5.50
LM0.08-873	0.08	873	33.8	30.6	1.7	12	73.1
LM0.12-873	0.12	873	28.2	30.7	1.3	1.6	96.2
LM0.16-873	0.16	873	23.7	31.1	2.2	0.5	84.7

Reaction conditions: temperature = 333K， methanol/oil =30:1, catalyst amount = 12 wt% (based on oil weight), reaction time =6 h, agitator speed = 400 rpm.

Table 2 lists the catalytic performances of solid base catalysts from recent literature and from the present work. LM0.08-873 is the most stable solid base catalyst. The catalytic activity of LM0.08-873 is next to the $LiNO_3$/MgO reported by MacLeoda et al. [13]. But, the Li leaching of the $LiNO_3$/MgO was as high as 98 ppm, indicating that amount of pure metal species dissolved into the polar phase (methanol) and formed methoxide lithium as the homogeneous catalyst. Thus biodiesel yield was promoted due to

the superior mass transfer for this homogeneous catalyst. Compared to the catalysts reported so far, LM0.12-873 exhibited an excellent performance and showed great potential in industrial application.

Table 2 Comparison of the catalytic performance of solid base catalysts for biodiesel reported in the literature and obtained in the present work.

Catalyst	Reaction Temperature (K)	Reaction time (h)	MeOH/oil molar ratio	Conversion (%)	Yield (%)	Metal leaching (ppm)	Reference
LM0.12-873	333	6	30:1		96	Li 1.3 Mg 1.6	At present
MgO	343	2	4:1	95	92	Mg 250	[11]
MgO	333	6	30:1	80		Not mentioned	[12]
MgO-Li_2O	338	2	9:1		89	Li : 200	[6]
$LiNO_3$/MgO	333	3	6:1		97	Li : 98	[13]
CaO	343	2.5	9:1		93	Ca :1200	[14]
CaO	348	2	4:1	72	65	Ca :325	[15]
CaO	338	2	15:1	99		Ca :139	[16]
CaO-CeO_2	373	6	30:1		90.0	Not mentioned	[9]
MgO-TiO_2	423	6	50:1		79.1	Mg: 23 Ti: 29	[8]

3.2. Characterization

The morphologies of the templated catalysts were investigated using SEM. As shown in Fig. 1, each catalyst exhibited a three-dimensional interconnected highly porous structure with bimodal pore distributions, i.e. mesopores of 10–200 nm and macropores of 1–4 μm. The macropores allows bulky triglycerides deeply penetrate and approach to the active site on the inner catalytic surface by mass transport, while the mesopore have a large specific surface area [9]. The synergistic effect of macro- and mesopores on the templated catalysts functioned efficiently as a catalyst for transesterification.

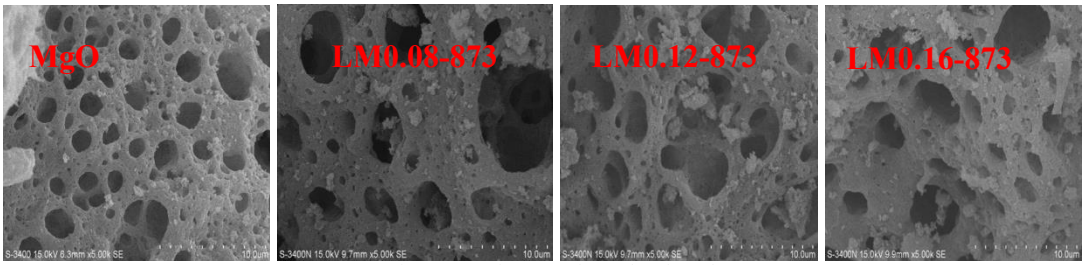

Fig. 1. SEM images of templated catalysts.

Fig. 2 shows the XRD patterns of the templated catalysts with various Li contents. For all samples, the diffraction peaks due to rock-salt MgO are clearly seen. The $Mg_2(SiO_4)$ phase was detected by XRD in LM0.08, LM0.12 and LM0.16, suggesting that MgO reacted with Si species during the thermal treatment of catalyst preparation. The addition of Li species promotes the formation of $Mg_2(SiO_4)$ phase. No crystalline Li-containing phase was detected by XRD in LM0.08 and LM0.12. For LM0.16, an incipient Li_2O hydrate phase was observed. It is well known that the close ionic radius of Li^+ ($r_{Li}{}^+$ =0.76 Å) compared with that of Mg^{2+} ($r_{Mg}{}^{2+}$ =0.72 Å) allows for easy substitutional accommodation within the MgO lattice [10]. For LM0.08 and LM0.12 with the low Li contents, after a thermal treatment, most of Li^+ ions likely diffuse in MgO crystallite, thereby inducing defects that are important for heterogeneous catalysis [10]. The diffusion of Li^+ ions gives rise to the absence of diffraction peaks corresponding to Li-containing phase. For Li/Mg molar ratio more than 0.16, excess Li ions form separated Li_2O phase.

The XPS binding energies (BE) for oxygen were measured for templated catalysts to reflect the basic strength of the oxygen. It has been reported that as the O1s BE decreases, electron pair donation becomes stronger and the basic strength increases [18]. As shown in Fig. 3, the BE of O1s decreased with the increase in Li content. This decrease indicates an increase in the basic strength of templated catalysts,

which most likely results from the lattice distortion and defects created by the substitution by the Li ions in MgO lattice. The catalyst of M0.16-873 show the lowest of O1s BE at 530.5 eV.

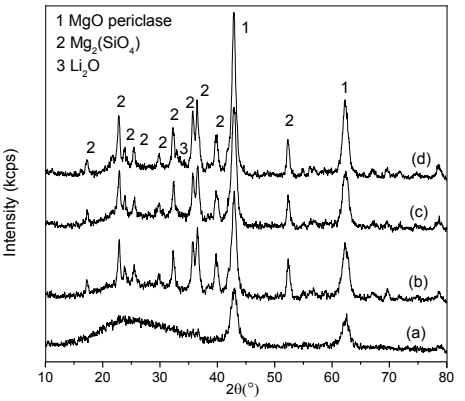

Fig. 2. XRD patterns of templated catalysts.

Based on the study by Wen et al. [6], the CO_2 desorption peaks of Fig. 4 can be divided into three groups exhibiting weak (CO_2 desorption between 293 K and 433 K), medium (CO_2 desorption between 433 K and 573 K), and strong basicity (CO_2 desorption between 550 K and 700 K). A CO_2 desorption peak was observed at around 800 K in LM 0.12-873 and LM0.16-873, which can be assigned to incipient decomposition of a reconstructed three-dimensional carbonate [10]. In fact, samples with high Li loadings form bulk carbonates when exposed to even ambient CO_2. Thus, the area under the peak above 650 K has not been taken into account for quantifying basic strength and base site density. As shown in Fig. 4, formation of strong base sites was particularly promoted when the Li/Mg molar ratio increased from 0.08 to 0.12. As mentioned above, the addition of Li species promoted the formation of $Mg_2(SiO_4)$ phase which is unfavorable for biodiesel synthesis because $Mg_2(SiO_4)$ phase is inactive. On the other hand, Li^+ ions diffuse in MgO crystallite, thereby inducing defects that are favorable for biodiesel synthesis. Therefore, there is most likely a critical value, beyond which the reaction of Mg and Si species approaches equilibrium and the amount of strong base sites increases remarkably. When the the Li/Mg molar ratio reached 0.16, amount of carbonate species were formed on the catalyst surface, resulting in a decrease of the strong base sites (see Fig. 4(a)). In addition, the BET decreased with the increase of the Li/Mg molar ratio (see Table 1), further lowering down the amount of strong basic sites of LM 0.16-873. In correlation of the CO_2-TPD results shown in Fig. 4 with catalytic activities presented in Table 1, it is clear that the most active catalyst of LM0.12-873 exhibited the largest amount strong base sites.

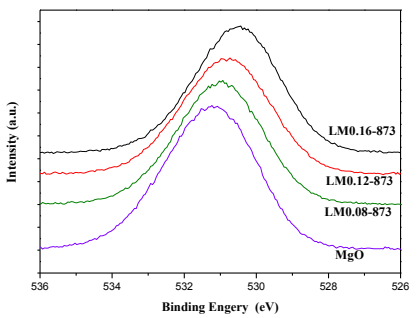

Fig. 3. XPS of templated catalysts.

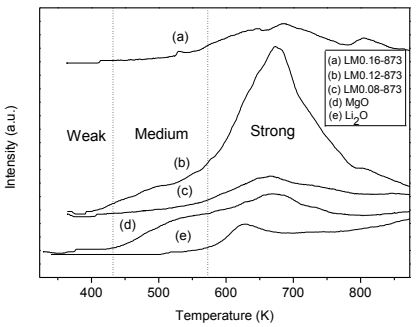

Fig. 4. TPD of templated catalysts.

4. Conclusion

On balance LM0.12-873 exhibited the best anti-leaching performance with next to the lowest Mg and Li leaching values, suggesting that the removal of the soluble metal species to purify the produced biodiesel are not needed any more. Templated catalysts exhibited a three-dimensional interconnected highly porous structure with bimodal pore distribution, which functioned efficiently for transesterification. The basic strength of MgO-Li_2O catalysts was enhanced due to the lattice distortion and defects created by the substitution by the Li ions in MgO lattice. The catalytic activities of MgO-Li_2O depend on the amount of strong base sites with the most active catalyst of LM0.12-873 exhibiting the largest amount strong base sites.

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